

Molecular Layering of Polydimethylsiloxanes at the Solid-Liquid Interface

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Introduction: The physical properties of confined liquids are different from those of the same liquid in the bulk [1]. Geometrical confinement by a hard wall should induce layering of thin liquid films at the solid-liquid interface and evidence of such layering obtained by x-ray reflectivity (XRR) has been reported recently [2-4]. In this work we have used XRR to look at thin liquid films of polydimethylsiloxanes (PDMS) of low molecular weights.

Methods and Materials: The PDMS samples used were a commercial product of Gelest, Inc. Co., and used as received. The molecular weights of the samples were 550 (DMS-TO3), 770 (DMS-TO5), and 2000 (DMS-TO12). The substrates, silicon (111) with native oxide, were cleaned in strong oxidizer. We spread thin films by making dilute solutions of PDMS in hexane (3 to 20 g/l), dipping the substrates in the solutions, and withdrawing them at 1.5 mm/s. The liquid films we studied were ~40-90 Å thick. For XRR measurements a Huber four-circle diffractometer was used in the specular reflection mode. The beam size was 0.4 mm vertically and 1.5 mm horizontally. The off-specular background was measured and subtracted from the specular counts.

Results: Figure 1 shows normalized reflectivity data (R/R_F) from typical scans of different PDMS films (R_F is the Fresnel reflectivity for the ideal interface). XRR data have been analyzed using a Fourier method that is useful for analysis of reflectivity data from low-contrast layer systems [4-5]. Before Fourier transforming of R/R_F and obtaining $P(z)$, the data were extrapolated to 4 Å^{-1} using a Gaussian in order to reduce termination effects. The Patterson functions $P(z)$ for some PDMS films are shown in Fig. 2. The positions of peaks of $P(z)$ correspond to the distances between regions where the density is changing. The large primary maximum is due to the solid-liquid and liquid-gas interfaces, i.e. its position indicates the overall thickness of the film. The existence of secondary maxima shows that there are density variations inside the liquid films. The positions of the secondary maxima in the Patterson functions reveal a periodicity of 8-10 Å (samples DMS-TO3 and DMS-TO5) that is consistent with the sizes of these PDMS molecules. For DMS-TO5 there is a characteristic small increase in the period of $P(z)$ oscillations as a function of z that can be related to the larger conformational freedom in packing of molecules with longer molecule chains. Further increasing the molecular weight of samples leads to suppression of $P(z)$ oscillations (DMS-TO12) causing the electron density profile to become more uniform.

Conclusions: Evidence of molecular layering is obtained for thin films of lowest molecular weight PDMS. The conformation of molecules of these samples can be characterized as an ellipsoid with axes 1:1.3:1.5 that is close to spherical shape and exposes the density variations in corresponding films. The length of PDMS chain increases with increasing of molecular weight which leads to extended conformation of molecules (possibly a more flat-like than bulk-like conformation is presented) and suppresses density variations in PDMS film ("smearing" of the electron density distribution normal to the reflecting surface).

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References: [1] J.C. Henniker, Rev. Mod. Phys. **21**, 322 (1949); [2] W.J. Huisman et al, Nature **390**, 379 (1997); [3] A.K. Doerr et al, Physica B **248**, 263 (1998); [4] C.-J. Yu et al, Phys. Rev. Lett. **82**, 2326 (1999); [5] O.H. Seeck et al, Appl. Phys. Lett. **76**, 2713 (2000).

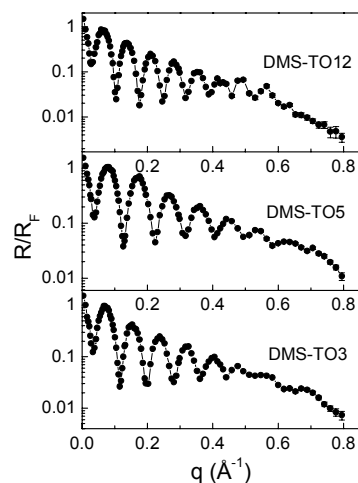


Figure 1. XRR data from ~70-90 Å PDMS films of different molecular weight.

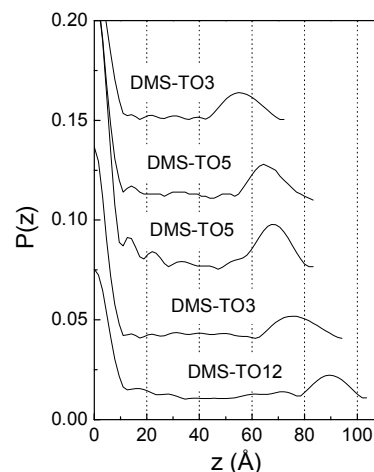


Figure 2. Patterson functions for PDMS films from the observed reflectivity, shifted vertically for clarity.